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ON THE

HEAT VALUE OF MILK.

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S Y N O P S I S .

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Introductory.

Milk may be defined as the fluid secreted in the lacteal gland of female mammals for the nourishment of their young. This definition is satisfactory enough from the scientific point of view if we add that the animals should be healthy. In other words, we are not to understand by milk any fluid which can be squeezed from the teat of the female. Pus might be so obtained in certain states, and while it would fulfil the first condition of the definition, it would be worse than useless for the nourishment of the young, and it would not occur in a healthy animal.

Cow's milk occupies a position of paramount importance as an article of diet. It contains all the elements requisite to maintain proper nutrition, and although it can hardly be called a perfect food, it approaches that ideal more than any other article of diet. Thus dietetic and commercial considerations come in, and the simple definition given above is not sufficient. It is necessary to have some standard by which to judge of the quality of the milk offered for sale. Cases of wilful adulteration are not uncommon, and this, in conjunction with the fact that cow's milk has so often to take the place of mother's milk in the nursing of the infant, emphasises the desirability of, and indeed the necessity for some legal standard.

The necessity is admitted on all sides. The difficulty is to determine what the standard is to be. The difficulty is a very real one. Nature, it is said, delights in variations. The truth of the aphorism is amply borne out in the case of milk, for analysis of milks of different cows, or even of milks of the same cows at different times, afford striking differences. The variations are so great that in the Farmer's Bulletin on "Milk as a food", published by the United States Department of Agriculture, it is said "it is entirely possible that one man may pay nearly twice as much as his neighbour for the same amount of nutriment when both buy milk at the same price per quart". The quality of the milk depends on many things and to a great extent the variations are unavoidable. Thus it is known that some breeds of cows yield quantity, others quality; the morning milk is usually larger in quantity, but poorer in quality; and the poorest milk is yielded in the spring. The age, the feeding and the housing of the animal are also important factors in determining the quantity and the quality of the yield of milk.

We, therefore, require to have something more definite than "the fluid secreted in the lacteal gland of the cow". The natural definition must give way to a more or less artificial one. A purchaser is entitled to receive the article for which he asks and pays, and in the case of milk, he ought to receive a fluid approximating in composition to the normal article. If this be admitted, then the only possible definition would seem to be one stating what the normal article really is. Such a definition can only be obtained after an analysis of many samples of milk taken from healthy animals under varying conditions. In this way one arrives at a correct idea as to the average composition of milk and after making due allowances, a limit is fixed,below which no milk offered for sale should fall. Such is the basis of the present legal standard of milk.

The only objection that can be urged is that on occasion an apparently healthy cow will give milk which is below the legal standard, and it is held to be a hardship that the vendor should be punished for selling milk which satisfies the natural definition. These abnormal milks are rare, and in any case, commercially, milk is almost invariably the mixed milk of a herd and therefore the low milk of one cow will be counterbalanced by the mixture of extremes.

The position adopted by the state is perfectly logical. Milk is defined as a fluid of a certain composition and the vendor is held responsible for what he sells. If he sells milk which falls below the standard fixed on an analysis of many thousand samples, he must suffer the consequences.

PRESENT LEGAL STANDARD OF MILK.

At the present time the fat of milk is taken as the guide to its quality. There are several reasons why it should be. It is in the first place one of the most important constituents of milk from the dietetic point of view. Commercially it is the most important because it is the most valuable. It is, therefore, frequently abstracted by the dishonest dairyman. Further, it can be estimated chemically with ease and exactness, compared to the estimation of the other constituents.

There is, however, great difference of opinion as to what proportion of fat should be insisted on. In connection with this, it is necessary to know the average composition of milk and in the pages of "The Analyst" will be found from time to time reports of the analyses of many thousand samples of milk. The average composition is stated in the Analysis of Food and Drugs by Pearmain & Moore to be as follows. This average corresponds closely with those given in The Analyst by Bell, Vieth, Richmond and many others.

Water	=	87·6
Fat	=	3·6
Sugar	=	4·8
Proteid	=	3·3
Ash	=	0·73

The great bulk of opinion adopts the view that unadulterated milk rarely gives less than 3·5 per cent fat and 8·5 per cent solids-not-fat. The standard adopted by the Inland Revenue Department was till lately much lower:-

Total Solids	11·25%
Fat	2·75%
Solids-not-fat.	8·5%

In 1900, as the result of much agitation, a Departmental Committee was appointed by the Board of Agriculture. It presented a Report recommending a governing limit of 3·25 per cent fat, and 8.5% solids-not-fat. These limits were not adopted, but the President of the Board of Agriculture issued regulations in 1901 requiring milk, in order to be considered genuine, to contain not less than 3% fat and 8·5% solids-not-fat.

The solids-not-fat are not further subdivided. No attention is paid to the amount contributed by the individual constituents - proteid, lactose, ash. Vieth has shown that in genuine milk they are commonly in the following proportion - sugar 13, proteid 9, ash 2. Adopting this division the present legal standard for genuine milk is:-

Fat	3·0
Sugar	4·6
Proteid	3·2
Ash	·7.

The sugar, proteid and ash together making 8.5%.

MILK AS A FOOD.

Physiologically the value of all foods depends chiefly on two things - how far will they serve to build up and repair the tissues, and how much heat will they produce in the body. Other considerations are involved, and they must not be neglected. The digestibility, the palatability and the cost are factors which cannot be ignored, but,granting these qualities, the important points are as stated above. The percentage of proteid is the measure of the first and the total caloric value, provided the food is wholly absorbed, is the measure of the second.

If we look at milk as a food, its right to be regarded as one of the best we have cannot be disputed. It contains all the necessary elements to maintain nutrition and in addition it fulfils the conditions of digestibility and palatability. It also ranks high both as a tissue builder and as a producer of heat.

Chemical analysis affords the means of judging of the value of milk in respect of the last mentioned functions. The percentage of proteid can be determined, and this directly gives the indication of the place milk occupies as a tissue builder.

To arrive at the caloric value, the process is more indirect. The separate constituents have to be estimated by chemical analysis. It is then necessary to multiply the percentage of each constituent by the caloric value of each. The caloric value of a gramme of proteid, a gramme of carbohydrate and a gramme of fat have been fixed by experiment, and if one multiplies the amount of each constituent present in a known quantity of milk by its known caloric value, and adds the totals together, one arrives at the total caloric value of the sample of milk.

The above method may well be called the indirect method of calculating the caloric value. The bomb-calorimeter gives us a direct method of estimating the caloric value of the sample of milk. It does away with the necessity of the preliminary chemical analysis,for the milk is dried and then incinerated in the calorimeter, and from the readings of the thermometer, we calculate the heat valve of all the milk solids at one operation.

The bomb-calorimeter is an instrument which has not yet come into general use in this country, and the first object of this research was to test the accuracy of the results obtained by the calorimeter. Milk was the article chosen for this purpose. Next, it was intended to estimate the heat value of samples of milk in conjunction with chemical analysis in order to show the relationship of the total heat value to the constituents. Lastly, it appeared probable if the calorimeter yielded accurate results that the caloric value of milk would afford a suitable basis for a legal limit or standard. The present legal standard is based on the amount of one constituent, whereas a standard based on the caloric value, as estimated by the calorimeter, is a measure of the quality of the principal constituents of milk. The rationale of the method is simple. If the total solids are deficient, the heat value will also be deficient, and if this deficiency is so marked that the heat value falls below a fixed limit or standard, the milk will be considered to be adulterated.

THE BOMB CALORIMETER.

The principle of the bomb calorimeter depends on the completeness and the rapidity of the combustion. A high pressure of exygen is used in the incineration, and the water in the calorimetric vessel attains its maximum temperature in a very short time. The loss by radiation is, therefore, small and what loss there is can be calculated by noting the rate at which the water cools after having attained its maximum.

It is difficult to convey any idea of the instrument in writing and without illustration. I shall merely mention the different parts. Outermost there is the waterjacket which is made of copper. It is 13 inches high and 2 inches broad, and it encloses a circle of 7 inches diameter. In the space bounded by the waterjacket goes the calorimetric vessel. It is made of tin, is 9 inches high and 5 inches in diameter. The water which is placed in this vessel has its temperature raised by the incineration.

The bomb is a strong metal vessel lined with a special porcelain. It has a lid which screws down and fits very exactly. There are two openings passing through the lid - the inlet and the outlet for the oxygen. The inlet opening has a tube passing into the bomb and this acts an electrode. The platinum capsule containing the material to be incinerated is attached to this electrode. The second electrode passes through the centre of the lid. The bomb is placed in the centre of the calorimetric vessel.

The mixer is used to maintain an equable distribution of the heat in the water around the bomb.

The Beckmann Thermometer is placed in the water round the bomb. It is finely graduated and the readings are taken with a magnifying glass. The temperature can be read to the third decimal place.

During combustion the hydrogen combines with oxygen to form water, the carbon forms carbonic acid, the sulphur sulphuric acid, etc. Heat is evolved by the formation of the acids and their combination with water, and a correction has to be made on account of the heat obtained in this way. It is known that one c.c. fifth normal acid yields three calories on its combination with water. On the completion of the incineration the interior of the bomb is washed with distilled water, and the acid is then titrated with fifth normal soda. One can thus tell how much heat has been produced by the acids and subtract it from the total caloric value. The error due to this cause is very small and might almost be disregarded.

A further correction has to be made for the iron wire which passes between the two electrodes and completes the circuit. The heat value of this wire was experimentally determined and deducted from the total heat value.

The details of the experiment may now be given. Ten c.c. of the milk are carefully pipetted into a clean platinum capsule, and dried in a water oven. Hitherto it has been customary to drop the milk on to a cellulose block to make sure of incineration. This entails the determination of the heat value of the cellulose, the weighing of the cellulose block and subsequent subtraction of the heat value of the cellulose block from that due to the block plus the milk. In the course of the experiments recorded in the following pages, no difficulty was experienced in obtaining complete combustion of the milk when it was placed in the capsule and thoroughly dried. Of course the direct estimation without cellulose blocks is simpler and probably more correct for it admits less liability of error.

The water in the calorimeter vessel is tested with the Beckmann thermometer to see whether the thread is at a suitably low point to allow of the full rise of three to four degrees being registered. The vessel and the water are carefully weighed, and made up to a known weight with distilled water. The vessel and water are then placed within the waterjacket. Two thousand five hundred c.c.of water were used in the estimations given below.

The platinum capsule with the dried milk is fixed on to the inlet tube of the lid described above. To the same tube is attached the fine iron wire which serves to start the combustion - the other end being attached to the electrode which passes through the centre of the lid. A few c.c. of water - two c.c. - are then placed in the bomb to saturate the interior with aqueous vapour and the lid is screwed home.

The bomb is then filled with oxygen. This is done by attaching it to an oxygen cylinder. On the connecting tube is placed a manometer for registering the pressure. The tap of the cylinder is opened and both inlet and outlet of the bomb are kept open for a little so as to allow the air in the bomb to be displaced by the oxygen. The outlet is then closed and the pressure of oxygen allowed to rise gradually to twenty three atmosphere, when the cylinder tap is turned off, and the inlet closed also. The wires from the accumulator are attached to the electrodes on the lid and the bomb is placed in the water in the calorimeter vessel. The mixer is adjusted and the thermometer placed in position.

Readings of the thermometer are taken every half minute, and after a number have been taken to determine whether the temperature of the water in the calorimetric vessel is stationary, rising or falling, the current is allowed to pass for a third or a half second. This causes the iron to glow and burn with the oxygen. The burning oxide falls on the dried milk and starts the incineration. The temperature of the water rises, rapidly attains a maximum and then falls slowly.

Readings are taken every half minute and are continued for five minutes after the maximum has been reached, in order to determine the rate of fall and so arrive at the error which has to be allowed for loss by radiation.

The bomb is then taken out, dried and the lid unscrewed. The interior is washed with distilled water and the washings are titrated with fifth normal soda solution and in this way one is able to correct the error due to the acids. Every part of the bomb is carefully dried and this completes the experiment.

Below is given the record of a single estimation.

v.	t.	T.	t_1	v_1
	.252	.252	3.362	
	.252	2.220	3.360	.002
	.252	3.132	3.354	.006
	.252	3.315	3.349	.005
		3.360	3.342	.007
		3.370	3.338	.004
		3.370	3.331	.007
			3.328	.003
			3.321	.007
			3.318	.003
			3.312	.006

In the above table v equals the differences in the readings before incineration. In this case there were none as is shown in column t where are recorded the readings before incineration begins. In column T the half-minute readings from the time the current is switched on are given. It will be seen the temperature of the water rose from 0.252° to 3.370°. The fourth column t_1 records the readings of the thermometer when it has commenced to fall. The last column v_1 gives the difference between the successive readings in the fourth column.

The first step in the calculation is to calculate the loss caused by radiation, and for this purpose the following formula is used:-

$$\frac{v - v_1}{t_1 - t}\left(\frac{T_2 - T_1}{9} + \frac{T_1 + T_n}{2} + \sum\frac{T}{1} - nt\right) - (n-1)v$$

In the above experiment v = 0, v_1 is the average of the figures in the last column and is ·005; t is the average of the figures in the second column and is ·252; t_1 is the average of the figures in the fourth column, minus the original temperature of the water and is 3.085; n is the number of readings in the column T; T_1 is the first reading in the column T and is ·252; T_2 is the second and is 2·220; T_n is the last and is 3.370; $\frac{T}{T}$ means the summation of all the figures in column T with the exception of the last.

If these numbers be substituted in the formula and the sum worked out, it will be found to be .022° and that is the amount of heat lost by radiation. It has consequently to be added on to the total heat produced.

To ascertain the total heat, it is necessary to subtract the original heat from the maximum, i.e. ·252° from 3·370° or 3.118°. To this has to be added the error due to radiation ·022°; thus we get a total rise of 3·140°. The problem comes to be -

10 c.c. milk raise 2500 c.c. water 3·140°, how much will 10 c.c. milk raise 1 c.c. of water. If this be worked out, it will be found that 10 c.c. milk will raise 1 c.c. 7850°, or in other words, will yield 7850 calories. It is necessary to deduct from this the heat value of the iron wire which was experimentally found to be 27 calories, and the heat value of the acids which in this case was 15 calories. (5 c.c. fifth soda were used to titrate the washings; each c.c. acid yields 3 calories: therefore proportion of heat due to the acids was 15 calories). We subtract the 27 and the 15 calories, and we get a total heat value of 7808 calories produced by the 10 c.c. or the heat value of the milk is 780·8 calories per c.c.

The experiment and the calculation may appear intricate. In reality the reverse is the case. The whole working of the calorimeter and calculation of the figures can be picked up very rapidly and no particular skill is required. Further, little time is occupied and this is one of the advantages which the calorimeter estimation of milk has over the chemical. With a little practice one can finish the incineration and subsequent calculation in from thirty to forty minutes.

DEGREE OF ACCURACY

IN ESTIMATIONS BY THE BOMB CALORIMETER.

The first set of experiments were undertaken in order to answer the question "What is the degree of accuracy in estimations of the physical heat values by the bomb calorimeter"? It was considered that on the answer to this question depended the possibility of the calorimeter providing a new method of estimating the quality of milk. Obviously if fine differences in the heat values cannot be detected by the calorimeter, it could not be regarded as sufficiently accurate to fulfil the requirements of a legal standard.

Samples of milk were procured at various dairies and were diluted with water in varying degrees. The amount of water was carefully measured and when it was added to the milk thorough mixing was ensured by stirring and shaking. Ten c.c. of the original milk and ten of the diluted were then taken and dried in platinum capsules. When thoroughly dried, they were incinerated in the calorimeter and the caloric value determined.

Below is a list of the experiments done in the manner described above. It ought to be stated that all the experiments are given, and there is no picking or choosing of favourable results. The only results omitted are those which were vitiated by incomplete incineration, due either to insufficient drying or to other causes.

Milk No.I.

10 c.c. original milk gave heat value of 676 cal. per c.c.
10 c.c. do. diluted 50% do. 337 do.

The diluted milk should have given heat value of 338 cal. per c.c. - difference between actual and what should have been, is therefore - 1 calorie.

Milk No.II.

10 c.c. original milk gave heat value of 753·5 cal. per c.c.
10 c.c. do diluted 50% do. 379·4 do.

The diluted milk should have given heat value of 376·8 cal. per c.c. - difference between actual and what should have been is therefore - 2·6 calories.

Milk No.III.

10 c.c. original milk gave heat value of 652·8 cal. per c.c.
10 c.c. do. diluted 10% do. 581·7 do.

The diluted milk should have given heat value of 586·8 cal. per c.c. - difference between actual and what have been is therefore - 5·1 calories.

Milk No.IV.

10 c.c. original milk gave heat value of 682·7 cal. per c.c.
10 c.c. do diluted 17% do. 579.2 cal. per c.c.

There was slight unconsumed carbon in the platinum capsule after incineration of the diluted milk. The diluted milk should have given heat value of 566·6 cal. per c.c. - the difference between actual and what should have been is therefore (error partly due to unconsumed carbon). 12·6 calories.

Milk No. V.

10 c.c. original milk gave heat value of 877·4 cal.per c.c.
10 c.c. do diluted 7½% do. 813·0 do.

The diluted milk should have given heat value of 811·5 cal. per c.c. - difference between actual and what should have been is therefore - 1·5 calorie.

Milk No.VI.

10 c.c. original milk gave heat value of 776 cal. per c.c.
10 c.c. do. diluted 8% do. 726 do.

The diluted milk should have given heat value of 717·6 cal. per c.c. - difference between actual and what should have been is therefore - 8·4 calories.

Milk No. VII.

10 c.c. original milk gave heat value of 650 cal. per c.c.
10 c.c. do. diluted 4% do. 623·6 do.
10 c.c. do. diluted 8% do. 585·4 do.

The milk diluted 4% should have given heat value of 624 cal. per c.c. - difference between actual and what should have been is therefore - 0·4 calories.

The milk diluted 8% should have given heat value of 598 cal. per c.c. difference between actual and what should have been is therefore, (partly due to unconsumed carbon) 12.6 calorie.

Milk No.VIII.

10 c.c.	original milk	gave	heat value of	868 cal.	per c.c.
10 c.c.	do.	diluted 5%	do.	829.4	do.
10 c.c.	do.	diluted 10%	do.	784.7	do.

The milk diluted 5% should have given heat value of 824·6 cal. per c.c. - difference between actual and what should have been is therefore - 4·8 calories.

The milk diluted 10% should have given heat value of 791·2 cal. per c.c. - difference between actual and what should have been is therefore - 6.5 calories.

Milk No.IX.

10 c.c.	original milk	gave	heat value of	683.5 cal.	per c.c.
10 c.c.	do.	diluted $6\frac{1}{2}$%	do.	628.4	do.
10 c.c.	do.	diluted 12%	do.	601.3	do.

The milk diluted $6\frac{1}{2}$% should have given heat value of 639 cal. per c.c.: There was slight unconsumed carbon remaining after incineration. The difference between the actual and what should have been is therefore - 10·6 calories.

The milk diluted 12% should have given heat value of 601·4 cal. per c.c.; the difference between the actual and what should have been is therefore - 0·1 calorie.

It will be seen that the assumption is made throughout the above experiments that the mixture of milk and water was complete. Granting this, it is easy to calculate what the heat value of the diluted milk should be if the degree of dilution and the heat value of the original milk are known. This calculation has been made and the estimations of the heat values by the bomb calorimeter are compared with those obtained by calculation. The difference between the actual, i.e. calorimeter results and the expected, i.e. the calculated results, are underlined.

Looking over these differences, they are found to be small. They vary from 0·1 calorie per c.c. to 12·6 calories per c.c., and it would appear that the error is independent of the degree of dilution. The difference might almost be neglected and they compare favourably with the error which is always allowed in chemical experiment. It is difficult to institute such a comparison, but a good general idea may be obtained in the following way. The total calories of difference between the actual and the expected are added together and an average error taken. The total calories correspondingly to these differences are similarly added and their averages obtained. The table showing these averages is given below:-

Differences in cal. per c.c.	Number of cal. per c.c.
1	338
2·6	376·4
5·1	586·8
12·6	566·6
1·5	811·5
8·4	717·6
12·6	598
·4	624
4·8	824·6
6·5	791·2
10·6	639
·1	601·4
12) 66 5	12) 7475 1
5 5	622 9

The average difference thus works out 5·5 calories per c.c. on an average total of 622·9 calories per c.c. The error may be stated as being ·8 calories for every hundred calories or ·8%.

That is the average error in the heat values estimated by the calorimeter. It is necessary now to find a common basis in order to compare it with a similar error in chemical analysis. We have such a basis in the fact that the heat value of the fat of milk is known and it is therefore possible to state percentages of fat in terms of calories and vice versa.

Suppose a milk is taken with 3% fat. The calorimetric calculations are all stated in terms of the c.c., and of course the fat must be reduced to the same unit. 3% fat is equal to ·03 gramme per c.c. It is generally accepted that Rubner's figure, viz. 9318 calories per gramme fat, is correct and if we transform ·03 gramme on this basis, it represents 279 calories. It has been shown above that the average calorimetric error is ·8 calories per hundred; apply this ratio of error to the 279 calories yielded by the ·03 gramme fat, and it will be found to be equal to 2·2 calories. Change this error from calories into grammes and it will be found that 2·2 calories is yielded by ·0002 gramme fat.

The calorimetric error has been applied to the amount of fat per c.c., and the result is that on a total of ·03 gramme fat, it amounts to ·0002 gramme.

It hardly requires to be stated that no chemist would claim to work accurately within these limits. The objection may be raised that the chemist does not analyse 1 c.c. of milk. The usual method of calculating the percentage of fat is that of Adams, and in it 5 c.c. are taken. In this case the margin of error is not so small, it amounts to 5 multiplied by ·0002 - in a 3% milk - or ·001 gramme. The error is still small and few chemists will promise to detect an error of ·001 gramme on a total of ·15 gramme, i.e. the amount of fat in 5 c.c.milk of 3% fat.

Even this test is favourable to the chemist. To get a complete comparison, he ought to analyse the amount of fat in an undiluted milk. Then on dilution with water and subsequent analysis, he ought to be able to get a result not more than ·001 gramme - if the original milk were 3% - from what the result should have been by calculation from the original milk and the percentage of dilution.

The important thing to emphasise, however, is the fact that the calorimeter does give results sufficiently accurate to enable us to use it as a means <u>of estimating directly the heat value of complex mixtures such as milk</u>. Its results are also sufficiently accurate to justify its use as a means of determining the quality of milk by its heat value. The chemical comparison has been dwelt on at length, and in this connection, it is interesting to note that in milk prosecutions it is rare to go beyond the second decimal place, and indeed, the first alone is commonly given in the analysis of the milk. It has been shown that the average error of the calorimeter is equal to an error of the fourth decimal place in chemical analysis. Therefore it is clear that, so far as accuracy is concerned, the results of the bomb calorimeter may be relied upon.

RELATION OF THE FAT TO THE TOTAL CALORIC VALUE.

As has been stated above, the amount of heat produced by one gramme of fat has been determined by Rubner, and his figure is so generally accepted that it was not thought necessary to do experiments with the view of condirming it. The object of the following experiments was to investigate the relationship of the fat to the total caloric value. In other words it was sought to answer the question:- "Is there a constant ratio between the percentage of fat and the total caloric value"?

A series of samples of milk was taken and the fat and the heat value of each were estimated.

The percentage of fat present was estimated by Adams' Method which is said to be the best method for obtaining accurate results. It is the official method of the Society of Public Analysts. Five c.c. of the milk are dropped on to fat free filter paper. The paper which is in a long strip is allowed to dry in the air, rolled into a coil and placed in an oven for a few minutes to ensure complete drying. The coil is then placed in the Soxhlet apparatus and the fat extracted with ether. The ether in all the extractions done was allowed to siphon over at least twenty times, and every care was taken to have the results as perfect as possible. When extraction was finished, the ether in the receiving flask was driven off and the fat which remained was brought to constant weight. The calculation of the percentage was simple - so much in 5 c.c. therefore so much per cent. In all the milks control experiments were done. In the same milks the total caloric value was estimated by the bomb calorimeter.

The following table is a record of the results obtained:-

	Fat Percentage.	Calories per c.c.
1.	5·4	888
2.	5·4	868
3.	5·3	829
4.	5·1	848
5.	4·9	784
6.	4·7	776
7.	4·3	726
8.	4·0	690
9.	3·9	663
10.	3·8	682
11.	3·3	683
12.	3·1	675
13.	3·0	628
14.	2·9	601
15.	2·8	607
16.	2·7	652
17.	2·6	566
18.	2·5	570
19.	2·1	540

These results show a general relationship between the fat and the heat value. This is what one would expect when on remembers that the fat yields about twice as many calories per gramme as either the proteid or the lactose. With a few exceptions the decrease in fat percentage is accompanied by a decrease in heat value. Such exceptions are number 4 and number 10. The point is this, however, that the decrease is general; there is not a constant ratio between the percentage of fat and the heat value. Milks numbers 1 and 2 are sufficient to show this, for in both there were 5·4% fat and there was a difference of 20 calories in the heat value.

Another interesting point is that the relationship is less definite as we go down to the lower percentages.

If we take a milk of 5·4% fat and assume that it produces 888 calories per c.c., and then calculate what the other milks should have yielded on this basis, the table works out as follows:-

No.	Percentage Fat.	Calories per c.c. by Calorimeter.	Calories per c.c. on basis of 5·4% Fat = 888 cal.	Difference.
1.	5·4	888		
2.	5·4	868		
3.	5·3	829	853	- 24
4.	5·1	848	820	+ 28
5.	4·9	784	805	- 21
6.	4·7	776	773	+ 3
7.	4·3	726	707	+ 19
8.	4·0	690	650	+ 40
9.	3·9	663	641	+ 22
10.	3·8	682	625	+ 57
11.	3·3	683	542	+141
12.	3·1	675	504	+171
13.	3·0	628	493	+135
14.	2·9	601	475	+126
15.	2·8	607	460	+147
16.	2·7	652	444	+208
17.	2·6	506	427	+139
18.	2·5	570	411	+159
19.	2·1	540	345	+195

The table shows that in every case, with the exception of number 3 and number 5, the calorimeter yielded more calories per c.c. than the calculation on the basis taken. The difference is not marked in the higher percentages of fat. It is when we go down the table to the milks with 3% fat and less that the discrepancy between the actual heat value as obtained by the bomb calorimeter and the heat value on the 5·4% basis becomes marked.

This discrepancy finds a probable explanation in the fact that variations in the total solids of milk are chiefly due to variations in the amount of fat. With a rise in the amount of fat, there is generally, it is true, an increase in the solids not fat, but the increase is slight. Thus Vieth has shown in a series of milks with total solids between 12·5% and 13% the increase in total solids not fat was only 0·1%.

Thus it is that with a decreasing percentage of fat the solids not fat occupy an increasing importance in relation to the heat value. The fat decreases, but therefore it does not follow that the heat value should decrease in the same ratio for the solids not fat are more or less stationary. It is in those milks with low fat percentages that the solids not fat contribute proportionally much more to the caloric value. The results obtained by the calorimeter confirm this and thus theoretically and practically the result is the same - that the discrepancy is most marked in low grade milks.

The comparison of the fat percentages and the total caloric value leads to the conclusion that no direct ratio can be established between the two.

RELATION OF THE TOTAL SOLIDS TO THE TOTAL CALORIC VALUE.

This was next investigated and a few experiments were sufficient to lead to the same conclusion as was found in the case of fat.

The total solids were calculated as follows:- 10 c.c. of the sample of milk were placed in a clean platinum capsule. The sample was dried in a water oven and brought to constant weight in a dessicator. The weight of the capsule being known, the weight of the total solids was obtained by subtraction.

	Total Solids Percentage.	Calories per c.c.
1.	14.4	868
2.	14.2	896
3.	13.0	812
4.	12.0	682
5.	12.0	650
6.	11.8	675
7.	11.2	607
8.	10.9	572

Examination of the table shows a very slight relationship between the results. If one sample be taken as the basis and the others calculated on it - similar to the fat comparison - a better idea is obtained of the extent of this relationship. No.4 is taken as the type.

	Total Solids percentage.	Calories per c.c. by calorimeter.	Calories per c.c. calculated on 12% = $68\frac{1}{2}$.	Difference.
4.	12·0	682		
1.	14·4	868	818	+ 40
2.	14·2	896	807	+ 89
3.	13·0	812	738	+ 74
5.	12·0	650	682	- 32
6.	11·8	675	670	+ 5
7.	11·2	607	636	- 29
8.	10·9	572	618	- 46

Theoretically one would expect such a result. The heat yielding products are the fat, the proteid and the lactose, and they are present in varying proportions. Their heat values are different and because of these variations, it is likely that milks with the same percentage of total solids would yield the same heat value. The table given above shows that the bomb calorimeter confirms the theoretical conclusion.

COMPLETE ANALYSIS OF MILK

IN RELATION TO THE TOTAL CALORIC VALUE.

The caloric values of the separate constituents of milk have been estimated by several workers, and it occurred to me that it would be interesting to compare the results obtained directly by the bomb calorimeter with those obtained indirectly, i.e. by chemical analysis and subsequent calculation.

For this purpose complete chemical analysis of the milks were carried through. The following methods were employed in the process.

The specific gravity was determined in two ways. The lactometer was first used and the reading obtained therefrom checked with the result of weighing the milk in a specific gravity bottle. Taken by itself, it is known that the specific gravity gives little indication as to the quality of the milk for cream, being lighter than water, lowers the specific gravity. The dairyman thus does a double fraud - he creams the milk and raises the specific gravity, he then adds water to the milk and brings the specific gravity back to the original.

The freezing point was taken in a series of milks as it was thought that it might yield valuable information as to the quality of the milk. The freezing point of a fluid depends on the nature and the quantity of substances dissolved in it, and not on those of bodies in suspension. It would seem, then, that the freezing point - although it would not be affected by the amount of fat present - might afford a clue to the quality of the milk because a milk with concentrated solids not fat, i.e. a milk which has not been watered, would lower the freezing point more than one that has.

The results were not satisfactory. The freezing point was lowered when there was a large amount of solids not fat, but the variation was general and no definite ratio could be established. For example, a milk with 8·2% solids not fat had a freezing point of 0·496°, and a milk with 8.9% had one of 0·558°. After a series of unsatisfactory results the experiments were discontinued. In connection with the freezing point of milk, it may not be out of place to quote the following from a paper by Ernest Beckmann in the Report of the 13th Assembly of the Bavarian Association of Chemists 1894:- "The reading of the thermometer is simple, but since an addition of 10% water only alters the freezing point by 5½ hundredths degree, it is to be feared that such a difference is too small to draw conclusions from when the results are not concordant."

The total solids were calculated in the way described on page 32 .

The percentage of fat was, as before, estimated by Adams' Method.

The amount of proteid was calculated by the following method:- 10 c.c. of the sample of milk were taken and made up to 100 c.c. with distilled water: sufficient Almen's Solution (Tannic Acid 5 gr, 25% Acetic Acid 8 c.c., 40 - 50% Alcohol 190 c.c.) was added to cause precipitation: 120 to 150 c.c. Almen's was usually added. The solution was left overnight and next day was filtered through a nitrogen free filter paper. The filter paper with the precipitate on it was then placed in a Kjeldahl Flask, and incinerated in the usual way with strong nitrogen free sulphuric acid. Thereafter, when incineration was complete, distillation was done with a 25% soda solution and the nitrogen driven over as ammonia into a flask containing fifth normal oxalic acid. The oxalic acid was titrated with fifth normal soda solution when distillation was complete, and thus one found the number of c.c. of oxalic used up by the ammonia. If this number be multiplied by 2·8, one obtains the amount of nitrogen in the 10 c.c. of milk and if the amount of nitrogen be multiplied by 6·37, one obtains the amount of proteid.

The lactose was estimated in this way:- 10 c.c. milk were taken and made up to 100 c.c. with distilled water; sufficient glacial acetic acid - 1 to 2 drops - was added to cause precipitation. Next day the solution was filtered and the precipitate washed with acidified distilled water. The filtrate was then boiled in order to precipitate the lactalbumin; after boiling it was filtered in order to remove the lactalbumin. The second filtrate was made up to a known amount - 250 c.c. - a definite quantity of Fekling's Solution was taken and the filtrate used to reduce it. In this way one determined the amount of lactose in the 10 c.c. of the milk taken and from this the percentage of lactose in the milk.

The ash was estimated by slow incineration of the solids found in 10 c.c. of milk.

As in all the previous experiments, control experiments were done to ensure accurate results.

The following table shows the result of the analysis stated in percentages.

	Total Solids.	Lactose.	Proteid.	Fat	Ash	Spec. Grav.	Cal. val.
Milk No. I.	10·83	4·25	3·08	2·66	·73	1030·0	572·0
" " II.	14·40	4·82	3·40	5·40	·74	1031·4	888·5
" " III.	10·82	4·18	3·26	2·50	·76	1030·0	570·8
" " IV.	11·76	4·48	3·34	3·10	·77	1031·9	669·4
" " V.	11·08	4·23	3·08	2·88	·76	1030·1	607·7
" " VI.	11·96	4·72	3·36	3·01	·73	1032·4	656·7
" " VII.	9·79	3·75	3·13	2·11	·72	1028·8	531·5
" " VIII.	12·01	4·21	3·06	3·82	·74	1030·2	682·7
" " IX.	13·10	3·80	3·49	5·10	·75	1029·1	812·6

The next step was to calculate the heat values of the samples of milk from their chemical composition. The heat values of the separate constituents have been given by different authorities.

The figure taken for fat was that of Rubner, viz. 9318 calories per gramme.

The heat value of casein has been variously stated. Danilewsky found that one gramme of casein yielded 5855 calories, and Stohmann gives two figures - 5867 calories per gramme and 5849. The three are very close and for the purpose of estimating the heat value of milk indirectly a mean was taken. The number 5860 calories per gramme is used in the following calculations. It ought to be stated that it is assumed in multiplying the proteid present by this number that lactalbumin has the same heat value as casein.

Rubner estimates the heat value of lactose as 3951 calories per gramme. Stohmann puts it at 3737 calories, and Rechenberg at 4162. If a mean be taken of the three we get the figure 3950 calories per gramme.

These are the constituents of the milk which contribute to the caloric value. The ash has, of course, no heat value.

The figures given are now applied to the milks which were analysed. The heat value, so obtained, is compared with the heat value of the milk as a whole.

Milk No.I.

Lactose	4·25 x 3950	=	16787·5
Proteid	3·08 x 5860	=	17462·6
Fat	2·66 x 9318	=	24785·8
			59035·9

The heat value of the milk, provided that the chemical analysis is correct, and that the correct values of the fat, proteid and lactose have been taken, is therefore 590·3 calories per c.c. If we turn to page 39 and look at the table given thereon, we see the bomb calorimeter gave the heat value as

572.0 calories per c.c. The difference is 18·3 calories per c.c.

Milk No.II.

Lactose	4·82 x 3950	= 19039·0
Proteid	3·40 x 5860	= 19924·0
Fat	5·40 x 9318	= 50317·2
		89280·2

The heat value by calculation is 892.8 calories per c.c. The heat value of the sample incinerated in the calorimeter was 888·5 calories per c.c. The difference is 4·3.

Milk No.III.

Lactose	4·18 x 3950	= 16511·0
Proteid	3·26 x 5860	= 19103·6
Fat	2·50 x 9318	= 23295·0
		58909·6

The heat value by calculation is 589·0 calories per c.c. The actual heat value was 570·8 calories per c.c. The difference is 18·2 calories per c.c.

Milk No.IV.

Lactose	4·48 x 3950	= 17696·0
Proteid	3·38 x 5866	= 19572·4
Fat	3·10 x 9318	= 28886·8
		66154·2

The heat value should be 661·5 calories per c.c. The estimation by the calorimeter was 669·4 calories per c.c. The difference is 7·9 calories per c.c.

Milk No.V.

Lactose	4·23 x 3950	=	16708·5
Proteid	3.08 x 5860	=	17873·0
Fat	2·88 x 9318	=	26855·8
			61417·3

The heat value should be 614·1 calories per c.c. The bomb calorimeter gave heat value of 607·7 calories per c.c. The difference is 6·4 calories per c.c.

Milk No.VI.

Lactose	4·72 x 3950	=	18644·0
Proteid	3·36 x 5860	=	19358·0
Fat	3·01 x 9318	=	28047·0
			66029·0

The heat value should be 660·2 calories per c.c. The actual heat value was 650·7 calories per c.c. The difference is 9·5 calories per c.c.

Milk No. VII.

Lactose	3·75 x 3950	=	14812·5
Proteid	3·13 x 5860	=	18394·4
Fat	2·11 x 9318	=	19660·9
			52867·8

The calculated heat value is 528·6 calories per c.c. The estimation by the calorimeter was 531·5 calories per c.c. The difference is 2·9 calories per c.c.

Milk No. VIII.

Lactose	4·21 x 3950	=	16629·5
Proteid	3·06 x 5860	=	17962·0
Fat	3·82 x 9318	=	35594.7
			70186·2

The calculated heat value is 701·8 calories per c.c. The bomb calorimeter gave the heat value as 682·7 calories per c.c. The difference is 19·1 calories per c.c.

Milk No. IX.

Lactose	3·80 x 3950	=	15010·0
Proteid	3·49 x 5860	=	20480·0
Fat	5·10 x 9318	=	47521·8
			83011·8

The calculated heat value is 830·1 calories per c.c. The bomb calorimeter gave the heat value of 812·6 calories per c.c. The difference is 17·5 calories per c.c.

Examination of these analysès proves that the two methods of calculating the heat value gave on the whole very similar results. The greatest difference recorded above is that of Milk No.VIII. where the error amounted to 19·2 calories per c.c. The closest approximation is to be found in Milk No.VII. where the difference was only 2·9 calories per c.c.

In the following table the difference and the total calories are averaged:-

18·3	590·3
4·3	892·8
18·2	589·0
7·9	661·5
6·4	614·1
9·5	660·2
2·9	528·6
19·1	701·8
17·5	830·1
9) 104·1	9) 6168·4
11·6	685·4

On the nine comparisons the average error was 11·6 calories on a total average of 685 4 calories per c.c., or a percentage difference of 1·7 calories. The difference is small and it must not be forgotten that the indirect method involves the chemical analysis of the milk, and in this way is more liable to error.

It is interesting to note that in every case the amounts of heat contributed by each constituent were in the same order. The fat of course was always the largest producer; the proteid came next and sometimes approximated to the fat; lastly the sugar contributed less than the proteid in all the samples of milk which were analysed.

The above comparisons of the heat values obtained by the calorimeter and by the indirect method were made before I came across a paper by Schlossmann in the Zeitschrift fur Physiologische Chemie Bd XXXVII. in which he had done the same thing. The heat values he adopted for the constituents were for fat 9318 calories per gramme; for lactose 3862 calories per gramme; the proteid was given as so many calories per gramme of nitrogen and the number he found for cows' milk was 3879 calories per gramme nitrogen. The records of only two analyses of cows' milk are given, but the difference between the heat values obtained by the two methods is remarkably small. In the two examples he gives the heat values as determined by chemical analysis and calculation were 713·9 calories per c.c. and 828·4 calories respectively, whereas the heat values by the calorimeter were 713·0calories per c.c. and 827·3 calories respectively. The differences were thus ·9 and 1·1 calories per c.c. They are less than the differences recorded in the series above and considering the sources of error - the complete chemical analysis of the milk, the estimations of the heat value of the constituents, and the estimation of the heat value of the sample - they say much for the carefulness with which the work was done.

PROPOSED LEGAL STANDARD.

The bomb calorimeter yields an accurate estimate of the total caloric value of milk. Because it does so, it is proposed that it should be used in settling the quality of the milk. The first step towards this is to fix a standard or limit below which milk, offered for sale, must not fall. The standard would of course be a stated number of calories per c.c.

It is hardly within the scope of this paper to fix such a number. All that was intended has been done - to show the possibility and suitability of this method of determining the value of milk. The exact number of calories per c.c. would be a bone of contention between the people who cry for a high standard and those who desire the low. The dispute is no new one. It exists at the present time for analysts hold that the present standard falls much below the average composition and therefore desire it raised while the other people interested, namely the farmers etc. resist any change.

If we apply the calculation method to milk of average composition (given on page 5) we find it comes out as follows:-

Lactose	4·8 x 3950	=	18960·0
Proteid	3·3 x 5860	=	19338·0
Fat	3·6 x 9318	=	33549·8
			71847·8

The total caloric value of 1 c.c. of average milk is, therefore, 718·4 calories. This could not be taken as the standard without raising the present standard to a considerable degree. It is to be assumed that there is not any likelihood of the standard being raised, merely because the basis of the standard is changed.

If we now take the milk which just satisfies the present legal standard (see page 6) and calculate its heat value, the result is as follows. It is assumed that Vieth's figures for the proportion of proteid, sugar and ash in the solids not fat are correct.

Lactose	4·6 x 3950	=	18170·0
Proteid	3·2 x 5860	=	18752·0
Fat	3·0 x 9318	=	27954·0
			64876·0

The heat value of milk which just satisfies the present legal standard is 648·7 calories per c.c. A transference of the present standard composition would, therefore, mean that by the suggested method the heat value of a sample of saleable milk would require to be 650 calories per c.c. or more. Below this limit the milk would be held to be adulterated and the vendor liable to prosecution.

COMPARISON OF PRESENT AND PROPOSED STANDARDS.

It is unnecessary to recapitulate the arguments which have been advanced above, for state interference in regard to the sale of milk. If anything further were required, one has only to look through the heat values of the milks which have been recorded in the course of this paper. It will be seen that they vary from 888 calories per c.c. to 540 calories per c.c. The milks were bought at various dairies in town and on each occasion sweet milk was asked for. It is evident that the purchaser of the former was receiving nearly forty per cent better value than the purchaser of the latter though the same price was paid for both.

The state interference resolves itself into the setting up of a standard or limit by which the quality of the milk offered for sale is judged. The present standard is based on the determination by analysis of the percentage of fat in the milk. It must be admitted that, looked at purely from the legal aspect, it affords a satisfactory means of ensuring that the public are not defrauded. It is, however, only a legal standard and it takes account of the amount of one constituent.

The rationale of the suggested standard has already been explained. It depends on the fact that milks vary in caloric value according to the amount of the different solids present. The proposed standard is not based on chemical analysis and no attention is paid to the amount of any or of all of the constituents. At the same time it is a measure of the constituents for it depends on the physical heat value which they can collectively produce. It is therefore a physiological and dietetic standard. The importance of the heat value of all foods has been emphasised in the foregoing pages. It is especially important relatively in the case of milk for the other important element, viz. the proteid, is the most stationary constituent of milk.

It is claimed for the proposed standard that it gives us the value of the sample of milk as a food and in this respect is superior to a mere statement of the fat percentage. It gives information of course only regarding the heat value. It tells us nothing of the tissue-forming powers of the milk, i.e. it gives no index of the proteid present. From the point of view of a complete knowledge of milk as a food the argument is valid enough. At the same time it is well to remember that the present standard gives neither the heat value nor does it take into account the amount of proteid present. Further, it is known that the proteid is the stationary constituent. Its average percentage is 3·3 and it may be said to vary between 3 and 3·5%. Fat is the constituent which varies the most, then comes milk sugar and lastly the proteid which in all except adulterated milks ranges from 3 to 3·5%.

The physical and physiological heat value of milk approximate closely. That means most of the milk is used up in the processes of digestion and absorption. This fact strengthens the claim of the proposed standard to be regarded as being founded on a better basis than the present. The total caloric value is a measure of all the solids in the sense that it gives their total value as food in terms of the heat they produce. It is the direct measure of the quality of the milk: the present standard is the indirect measure of the quality of the milk through the estimation of the quantity of one constituent.

It is claimed for the method of estimating caloric values by the calorimeter that it affords not only a dietetic standard, but also a legal standard as suitable as the present. It is only necessary to prove the accuracy of the results of incineration in the calorimeter to establish the possibility of its use for legal purposes. This has been done at length in a previous part of the paper. Granting the accuracy of the results, all that is then required is to fix the limit below which milk will be considered to be adulterated. The physical heat value is substituted for the percentage of fat, and if the former falls below the limit, the milk is adulterated in the eyes of the law just as much as if its percentage of fat were less than 3. It is to be clearly understood that the percentage of fat or any other solid is of no importance. The heat value which the solids collectively produce is the test of saleable or unsaleable milk. If one accepts the limit of 650 calories per c.c. (see page 48) then all milks below that limit are held to be adulterated. Applying this limit to the table on page 28 we see that milk No.13 yielded 628 calories per c.c. though it had 3% fat. It would, therefore, have been held to be adulterated in spite of the percentage of fat. On the other hand, milk No.16 with 2·7% fat gave caloric value of 652 and it would therefore have passed the standard. In every other case the result of the proposed standard would have been to corroborate the present. The two cases given show the importance of the lactose and the sugar in the milk. The proposed method takes account of them, the present disregards them in the sense that it puts them with the ash as solids not fat.

The difficulty of abnormal milks remains. The calorimeter does not claim to distinguish between a genuine poor milk and one that is poor owing to adulteration. There exists, however, no method of conclusively determining which is which. The present method of milk analysis does not do so. The cases on record of healthy cows under normal conditions yielding milk with less than 3% fat are not numerous. Just because of this rarity it is a reasonable position to insist that all samples which fall below the limit are to be considered adulterated. The limit has been fixed on the estimation of many thousand samples of milk and if the standard is to be effective in affording protection to the public, the vendor must be held responsible for the milks he sells and if that milk is below the limit - whatever the cause- he ought to be punished.

The proposed standard has been shown to have other advantages over the present. The working of the calorimeter has been described on page 10. The estimations can be rapidly and easily carried out. The present method necessitates chemical analysis of the fat and the determination of the total solids. In this more time is involved than in the use of the calorimeter. Further, chemical analysis, to ensure accuracy, must be done by experienced chemists. The bomb calorimeter demands no chemical knowledge and no particular skill. One could work it with a day's practice. In the paragraph on the bomb calorimeter, it has been shown that the estimation is simpler and can be done in a shorter time than the chemical determination of the percentage of fat. It is also claimed that the liability of error is at least as small in the calorimetric estimation as in the chemical analysis.

S U M M A R Y.

The principal results of the work described in the preceding pages may now be summarised.

The first point taken up was the use of the bomb calorimeter and its accuracy. The experiments given show that the calorimeter gives accurate results.

Next, the relation of the fat and the total solids to the total caloric value was shown to be a general one . No definite ratio between them could be established.

One of the most interesting parts of the work was the complete chemical analysis of milk in conjunction with the heat estimations. This constitutes a special feature of the present paper for with the exception of the two experiments published by Schlossmann the experiments here given are the only ones, so far as I know, where full chemical analysis and direct heat value estimates were done on the same milk. It was shown how the calculation of the heat value after chemical analysis and the estimation by the calorimeter gave approximate results. This is an important point, for it proves that the calculation method may be trusted to give a very correct idea of the heat value. The milks of practically

every animal have been chemically examined, and from this examination one could arrive at a close approximation to the heat value by calculation if a calorimeter were not available. On the other hand, it affords further proof of the accuracy of the estimations by the calorimeter.

The suitability of the heat value of milk being used as a legal standard has been discussed at length. It is claimed that the bomb calorimeter gives a new method of judging of the quality of milk. The results are accurate and therefore the new standard claims to be as satisfactory from the legal standpoint as the present standard. It is besides the measure of the dietetic worth of milk and the estimation of the heat value can be more simply and more rapidly carried through than the chemical analysis of milk.

Accuracy of results, simplicity of method, rapidity of estimation and a dietetic standard which at the same time is fitted to fulfil legal requirements are the advantages which are claimed for the suggested method of determining the quality of milk by the amount of heat it yields on incineration in the bomb calorimeter.

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